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The enthalpies increments of the chemical elementsfor minerals of cancrinite group

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ABSTRACT

The chemical elements increments for experimental values of standard enthalpies $\Delta_f H^o$ for three cancrinite group minerals have been calculated by means of linear programming problems. The obtained increments have been used in calculations of $\Delta_f H^o$ values for nine minerals of cancrinite group with known thermodynamic properties. The mean error of calculations makes about 1 %. The estimations for some minerals with unknown enthalpies have been carried out.

KEYWORDS

Cancrinite group minerals;
Standard enthalpies offormation from the elements;
Linear programming.

INTRODUCTION

The minerals of cancrinite group represent a class of framework microporous aluminosilicates with confined water, alkaline and alkali-earth cations (basically Na and Ca) and anions - hydroxide, carbonate, oxalate, sulfate, phosphate, chloride[8]. These minerals are widely widespread in alkaline complexes as rock-forming and postmagmatic minerals and frequent phases accompanying the red mud from aluminium production industry[14].

Recently we have presented the some schemes of estimations the standard thermodynamic potentials for zeolites[16, 17, 15] with the use of linear programming problems. The aim of presented study is the application of these methods for calculations of enthalpies of formations from the elements for cancrinite group minerals.

METHODS

The cancrinite - $Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O$, cancrisilite - $Na_{7.17}Ca_{0.01}[Si_{7.26}Al_{4.70}Fe_{0.04}O_{24}](CO_3)_{1.05}(PO_4)_{0.04}(SO_4)_{0.01}(OH)_{0.21}\cdot 2.635H_2O$ and carbonate-oxalate cancrinite - $Na_{6.9}K_{0.1}Ca_{0.1}[Al_{5.4}Si_{6.6}O_{24}](C_2O_4)_{0.4}(SO_4)_{0.1}\cdot 3.6H_2O$ from Khibino-Lovozero alkaline complex have been chosen as calibration minerals with the values of standard enthalpies $\Delta_f H^o$ =-14490.0±16.0, -14302.0±17.0 and -14473.0±21.0 kJ/molerespectively which experimentally determined in works[9, 10].

For reactions of these minerals formation from oxides:

$$3.465Na_2O+0.540CaO+0.005K_2O+0.025Fe_2O_3+2.740Al_2O_3+6.470SiO_2+2.300H_2O+1.250CO_2=Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O \text{ (cancrinite)}, \quad (1)$$

$0.010SO_3+0.020P_2O_5+3.585Na_2O+0.010CaO+0.002Fe_2O_3+2.350Al_2O_3+7.260SiO_2+2.740H_2O+1.050CO_2=Na_{7.17}Ca_{0.01}[Si_{7.26}Al_{4.70}Fe_{0.04}O_{24}](CO_3)_{1.05}(PO_4)_{0.04}(SO_4)_{0.01}(OH)_{0.21}\cdot 2.635H_2O$ (cancrisilite), (2)

$0.10SO_3+0.05K_2O+3.45Na_2O+0.10CaO+2.70Al_2O_3+6.60SiO_2+3.60H_2O+0.80CO_2+0.60O_2=Na_{6.9}K_{0.1}Ca_{0.1}[Al_{5.4}Si_{6.6}O_{24}](C_2O_4)_{0.4}(SO_4)_{0.1}\cdot 3.6H_2O$ (carbonate-oxalate cancrinite) (3)

we construct the linear programming problems:

$x^* = \min\Delta_f H^o(x)x$, $Ax= b=abs(null(A))/2$, $x\geq 0$, (4)

where A – the stoichiometric matrix on chemical elements of systems; b - the vector of the material balance which has been written as absolute value of null-space of matrix A; $\Delta_f H^o(x)$ – the standard enthalpies for components x of reactions (1-3), their values are taken from databases of a program complex "Selector"[2] and works[9, 10, 7] and are presented in TABLE 1.

The solutions of problem (4) with the data (TABLE 1) represents the x* = 1 mole of reactions products (1-3) – the calibration minerals.

The direct problems (4) are conjugate to them duals:

$y^*=\max by$, $A'y\leq\Delta_f H^o(x)$ (5)

where ' - an index of transposing.

For nonsingular solutions x* and y* of problems (4) and (5) are fair equality:

$\Delta_f H^o(x^*)x^*= by^*$ (6)

which for reactions (1-3) represents the linear decomposition of enthalpies values on molal increments of chemical elements.

We have applied the additive scheme for estimations of standard enthalpies $\Delta_f H^o(k)$ of cancrinite group minerals - k under the formula:

$\Delta_f H^o(k) = Y(k)\, y^*$ (7)

where Y (k) - stoichiometric formula of a mineral k, y*- the dual solutions of problems (5) (Таб.2).

The errors of calculations on (7) were estimated by means of the formula:

$\delta = 2abs(H_1-H_2)/(H_1+H_2)$ (8)

where H_1 - the calculated values and H_2 - the published data (TABLE 3).

TABLE 1 : The values of standard enthalpies of formations from the elements for components x of reactions (1-3)

Components, x	$-\Delta_f H^o$, J/mole
Na_2O	414220
CaO	635089
K_2O	361500
Fe_2O_3	824084
Al_2O_3	1675725
SiO_2	910735
H_2O (iceI)	292746
CO_2	393505
SO_3	395720
P_2O_5	1470050
O_2	0
$Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O$	14490000
$Na_{7.17}Ca_{0.01}Si_{7.26}[Al_{4.70}Fe_{0.04}O_{24}](CO_3)_{1.05}(PO_4)_{0.04}(SO_4)_{0.01}(OH)_{0.21}\cdot 2.635H_2O$	14302000
$Na_{6.9}K_{0.1}Ca_{0.1}[Al_{5.4}Si_{6.6}O_{24}](C_2O_4)_{0.4}(SO_4)_{0.1}\cdot 3.6H_2O$	14473000

TABLE 2 : The chemical elements increments y* (J/mole) for standard enthalpies of calibration minerals in reactions (1-3)

y^*_{El} for reactions (1-3)	Ca	Na	K	Al	Fe	Si	C	S	P	O	H
1	-358195	-23878	-107355	-248127	67009	-87954	257867	-	-	-419316	15986
2	-472003	-52433	-	-330482	-8362	-183620	169352	231039	34459	-370293	-6413
3	-853790	-236895	-333401	-875698	-	-941640	-536795	-827898	-	0	-175539

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RESULTS AND DISCUSSION

To compare the dual solutions y* (TABLE 2) them have been presented as the bar diagrams (Figure 1-3).

Let's notice that comparing of dual solutions among themselves it is necessary to consider that making calibration minerals chemical elements differ in total. Besides for reaction (3) in reagents set there is an oxygen (O_2) that leads to other dual solution that for reactions (1) and (2) which have some similarity. For reaction (3) significant difference of y* components follow from constraint conditions of a dual problem (5) namely $2y_O \leq 0$ (J/mole) whence follows $y^*_O=0$. For reaction (1) y^*_{Fe}, y^*_C and y^*_H have the positive values as y^*_P, y^*_S and y^*_C for reaction (2).

For some mineral of cancrinite group with unknown thermodynamics properties the values of standard enthalpies have been estimated by means of (7). The results of calculations are presented in TABLE 4. The discrepancy inestimationsup to 5% underthree dual solutions for some minerals (pitiglianoite, biachellaite)is caused by absence ofcertainchemical elements in y* but theirs presence in the substances stoichiometry.

TABLE 3 : Comparison of calculated and published data for the standard enthalpies (J/mole) of cancrinite minerals group, in brackets - errors (8) in percentage, the bold font – calibration minerals in reactions (1-3)

Minerals	$-\Delta_f H^o$, J/mole (bibli.)	$-\Delta_f H^o$, calculated on (7) for reactions (1-3)		
		1	2	3
Cancrinite [Ogorodova et al., 2009] $Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O$	14490000	14490000 (0.00)	14565220 (0.52)	14475776 (0.10)
Cancrisilite [Ogorodova et al., 2009] $Na_{7.17}Ca_{0.01}[Si_{7.26}Al_{4.70}Fe_{0.04}O_{24}](CO_3)_{1.05}(PO_4)_{0.04}(SO_4)_{0.01}(OH)_{0.21}\cdot 2.635H_2O$	14302000	14279734 (0.16)	14302000 (0.00)	14136536 (1.16)
Carbonate-oxalate cancrinite [Olysuch et al., 2011] $Na_{6.9}K_{0.1}Ca_{0.1}[Al_{5.4}Si_{6.6}O_{24}](C_2O_4)_{0.4}(SO_4)_{0.1}\cdot 3.6H_2O$	14473000	14222056 (1.75)	14253766 (1.52)	14473000 (0.00)
Cancrinite [Ogorodova et al., 2009] $Na_6Ca_2[Si_6Al_6O_{24}](CO_3)_2\cdot 2H_2O$	15552000	15714581 (1.04)	15879562 (2.08)	15808728 (1.64)
Cancrinite [Liu et al., 2007] $Na_{7.771}[Si_{6.004}Al_{5.956}O_{24}](CO_3)_{0.881}\cdot 3.48H_2O$	14524070	14484089 (0.28)	14528055 (0.03)	14404848 (0.82)
Cancrinite [Ogorodova et al., 2009] $Na_6Ca_{1.5}[Si_6Al_6O_{24}](CO_3)_{1.5}\cdot 1.1H_2O$	14691000	14686834 (0.03)	14827987 (0.93)	14797465 (0.72)
Cancrisilite[Kurdakova et al., 2014] $Na_{8.28}[Si_{6.07}Al_{5.93}O_{24}](CO_3)_{0.93}(OH)_{0.49}\cdot 3.64H_2O$	14684000	14804207 (0.82)	14850291 (1.13)	14733297 (0.34)
Cancrisilite [Ogorodova et al., 2009] $Na_7[Si_7Al_5O_{24}]CO_3\cdot 3H_2O$	14268000	14249157 (0.13)	14282719 (0.10)	14218269 (0.35)
Kyanoaxalite [Olysuch et al., 2011] $Na_7[Si_6Al_6O_{24}](C_2O_4)_{0.5}\cdot 5H_2O$	14555000	14764698 (1.43)	14825528 (1.84)	14854483 (2.04)
Mean error %		0.73	0.91	0.80

TABLE 4 : The calculated on (7) standard enthalpies values (J/mole) for calibration minerals from reactions (1-3)

Minerals	$-\Delta_f H^o$, calculated on (7) for reactions (1-3)		
	1	2	3
$Na_{4.7}K_{2.6}Ca_{0.1}[Si_{6.1}Al_{5.9}O_{24}](SO_4)_{0.8}\cdot 2H_2O$pitiglianoite[1]	14607722	14016957	14340730
$Na_5K_{1.5}Ca[Si_6Al_6O_{24}](SO_4)(OH)_{0.5}\cdot H_2O$alloriite[3]	14984964	14527436	14709145
$[Si_{6.3}Al_{5.7}O_{24}][Na_2(H_2O)_2][Na_{5.7}(CO_3)_{0.9}(SO_4)_{0.1}(H_2O)_{0.6}]$cancrinite[3]	14683836	14746586	14671610
$[Si_{6.6}Al_{5.4}O_{24}][Na_{1.2}Ca_{0.4}(H_2O)_{1.6}][Na_6(CO_3)_{1.3}(H_2O)_{1.2}]$cancrisilite[3]	14290774	14299837	14226615
$Na_8[Al_6Si_6O_{24}](SO_4)\cdot 2H_2O$vishnevite[8]	14723049	14407499	14329247
$Na_{3.76}Ca_{2.50}K_{1.44}[Si_{6.06}Al_{5.94}O_{24}](SO_4)_{1.84}Cl_{0.15}(OH)_{0.43}\cdot 0.81H_2O$biachellaite[12]	16783670	16112563	16296474
$Na_7Ca[Al_6Si_6O_{24}](CO_3)_{1.5}\cdot 2H_2O$cancrinite[18]	14880223	14989227	14923436
$Na_{7.58}K_{0.12}[Si_{6.19}Al_{5.81}O_{24}](PO_4)_{0.47}(CO_3)_{0.22}(OH)_{0.02}(SO_4)_{0.01}\cdot 3.345H_2O$depmeierite[10]	14555579	14515052	14056475

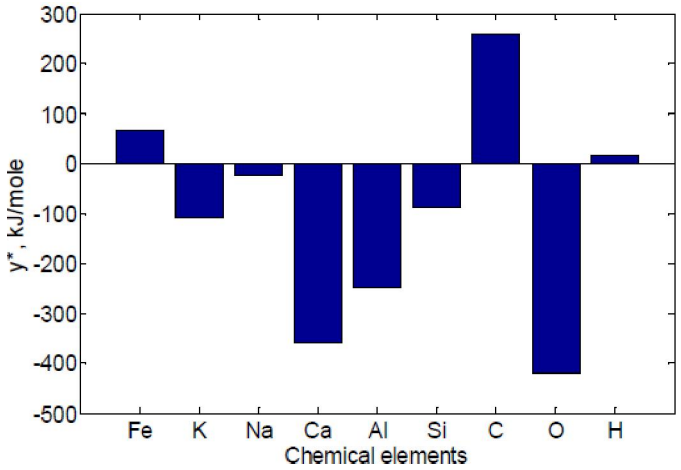

Figure 1 : The chemical elements increments of standard enthalpie value $\Delta_f H^o$=-14490.0 kJ/mole of calibration cancrinite mineral $Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O$[9]

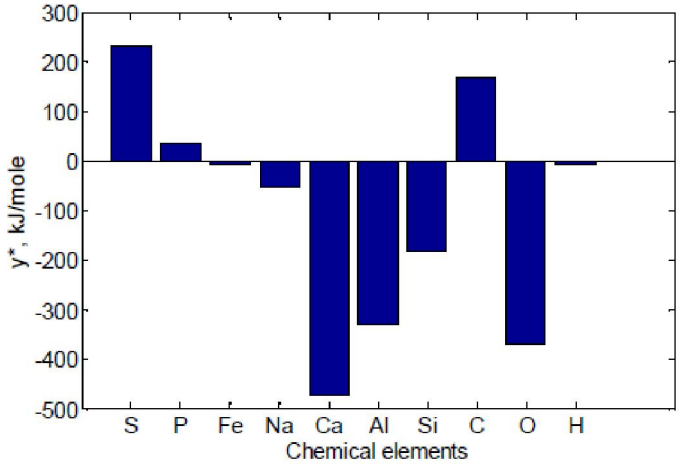

Figure 2 : The chemical elements increments of standard enthalpie value $\Delta_f H^o$=-14302.0 kJ/mole of calibration cancrisilite mineral $Na_{7.17}Ca_{0.01}Si_{7.26}[Al_{4.70}Fe_{0.04}O_{24}](CO_3)_{1.05}(PO_4)_{0.04}(SO_4)_{0.01}(OH)_{0.21}\cdot 2.635H_2O$[9]

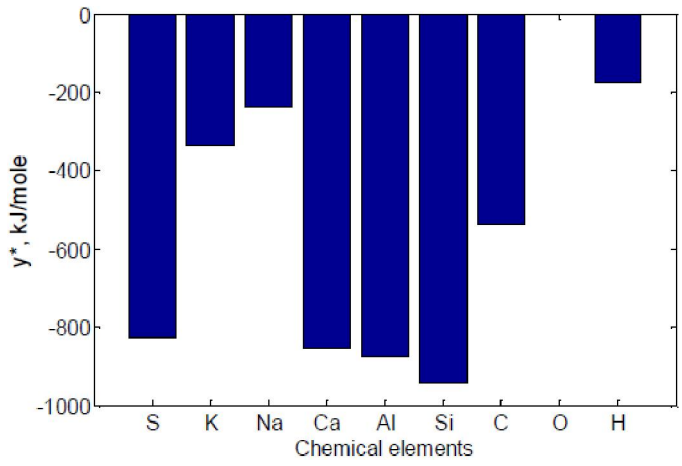

Figure 3 : The chemical elements increments of standard enthalpie value $\Delta_f H^o$=-14473.0 kJ/mole of calibration carbonate-oxalate cancrinite mineral $Na_{6.9}K_{0.1}Ca_{0.1}[Al_{5.4}Si_{6.6}O_{24}](C_2O_4)_{0.4}(SO_4)_{0.1}\cdot 3.6H_2O$[10]

Thus it is possible to expect more correct estimations in cases when the set of chemical element structure of calibration minerals and estimated substance coincide or differ slightly.

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The received values of chemical elements increments can be used for estimations of standard enthalpies of cancrinite group substances with prospective accuracy about 1-3 %.

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